



Rapid communication

Perchlorate uptake by salt cedar (*Tamarix ramosissima*) in the Las Vegas Wash riparian ecosystem

Edward T. Urbansky*, Matthew L. Magnuson, Catherine A. Kelty,
Stephanie K. Brown

*United States Environmental Protection Agency, National Risk Management Research Laboratory, Water Supply and Water
Resources Division, 26 West Martin Luther King Drive, Cincinnati, OH 45268, USA*

Received 24 March 2000; accepted 25 March 2000

Abstract

Perchlorate ion (ClO_4^-) has been identified in samples of dormant salt cedar (*Tamarix ramosissima*) growing in the Las Vegas Wash. Perchlorate is an oxidant, but its reduction is kinetically hindered. Concern over thyroid effects caused the Environmental Protection Agency (EPA) to add perchlorate to the drinking water Contaminant Candidate List (CCL). Beginning in 2001, utilities will look for perchlorate under the Unregulated Contaminants Monitoring Rule (UCMR). In wood samples acquired from the same plant growing in a contaminated stream, perchlorate concentrations were found as follows: $5\text{--}6\ \mu\text{g g}^{-1}$ in dry twigs extending above the water and $300\ \mu\text{g g}^{-1}$ in stalks immersed in the stream. Perchlorate was leached from samples of wood, and the resulting solutions were analyzed by ion chromatography after clean-up. The identification was confirmed by electrospray ionization mass spectrometry after complexation of perchlorate with decyltrimethylammonium cation. Because salt cedar is regarded as an invasive species, there are large scale programs aimed at eliminating it. However, this work suggests that salt cedar might play a role in the ecological distribution of perchlorate as an environmental contaminant. Consequently, a thorough investigation of the fate and transport of perchlorate in tamarisks is required to assess the effects that eradication might have on perchlorate-tainted riparian ecosystems, such as the Las Vegas Wash. This is especially important since water from the wash enters Lake Mead and the Colorado River and has the potential to affect the potable water source of tens of millions of people as well as irrigation water used on a variety of crops, including much of the lettuce produced in the USA. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Perchlorate; Salt cedar; Tamarix; Riparian ecosystem; Drinking water; IC; ESI-MS; Eradication

* Corresponding author. Tel.: +1-513-569-7655; fax: +1-513-569-7658.

E-mail address: urbansky.edward@epa.gov (E.T. Urbansky).

1. Introduction

Salt cedar (*Tamarix ramosissima*) is a woody plant, indigenous to Asia now found as an invasive species in western riparian (streambank) ecosystems (Westbrooks, 1998). Southwestern states experience the greatest effects due to the favorable climate (Muzika and Swearingen, 1999) with more than a million acres of land occupied (Deuser et al., 1998). *T. ramosissima* accumulates salt, which it then secretes through its leaves. This brackifies the nearby soil to the extent that native genera (e.g. *Salix*) cannot grow (Muzika and Swearingen, 1999). Because of the serious impact on native flora, projects to eradicate salt cedar have been undertaken by the Natural Park Service (Deuser et al., 1998). Tamarisks have colonized much of the land surrounding the Las Vegas Wash and can be found growing in shallow surface waterways, such as creeks or springs. The plant consumes and transpires incredible amounts of water so that it can bring about fluctuations in the local water table when it becomes active, roughly from March to December.

Perchlorate has been identified as a contaminant in the soil, surface water, and ground water of the Las Vegas Wash (Urbansky, 1998; Renner, 1999). The contamination in this region has been attributed to the production of ammonium perchlorate by defense and aero-space contractors dating back several decades (Damian and Pontius, 1999). Perchlorate's nature makes both potable water treatment and site remediation difficult (Urbansky and Schock, 1999; Espenson 2000). Perchlorate affects the thyroid (Wolff, 1998; Clark, 2000), and was placed on the Contaminant Candidate List (CCL) (Environmental Protection Agency, 1998; Perciasepe, 1998) and the Unregulated Contaminants Monitoring Rule (UCMR) (Browner, 1999). Water from the Las Vegas Wash flows into Lake Mead and becomes part of the Colorado River. Lake Mead and the downstream portion of Colorado River serve as the major source of potable water for southern California (including Los Angeles), southern Nevada (greater Las Vegas), and parts of Arizona. Consequently, the drinking water of tens of millions of people is potentially at risk. Moreover, Colorado River

water and other contaminated waters are used to irrigate farms that supply significant portions of the produce consumed in the USA. Therefore, this contamination has the potential to affect the nation's food supply if perchlorate is absorbed by food plants.

Because salt cedar influences the hydrology of the Las Vegas Wash and perchlorate salts are very water-soluble, it seems reasonable to consider whether salt cedar can take up perchlorate along with other salts.

2. Experimental section

Sections of tamarisk twigs, branches, and stalks ranging from 2 to 12 mm were collected from plants growing in the Las Vegas Wash. Samples were taken from sections of plant submerged in the water and from sections extending above the surface of the water. A mass of 80 g (wet mass) of the submerged stalks (3–12 mm diameter) was soaked in running deionized (DI) water for 2 min and then rinsed with a spray of DI water. A mass of 20 g (dry mass) of the exposed twigs (2–7 mm diameter) was similarly cleaned. Branch sections were shredded in a blender; and leached at 5°C for ~60 h; the plant matter to water ratio was 20 g dl⁻¹. The mixture was then suction filtered through Corning (Corning, NY, USA) 0.45-μm cellulose acetate with a glass fiber pre-filter.

Ion chromatography (IC) standards were prepared in DI water using sodium perchlorate (GFS Chemicals, Columbus, OH, USA). A stock solution containing 1000 μg ml⁻¹ was diluted as needed for spiking, constructing a calibration curve, and determining retention time. The collected shredded wood filtrates prepared at 20 g dl⁻¹ were diluted at a ratio of 1:6 v/v with DI water. The diluted solution from the submerged branches was cleaned up by passing a 5.0-ml aliquot through either Supelco (Bellefonte, PA, USA) Envi-Carb (carbon), Envi-Chrom P (polystyrene), or Waters (Milford, MA, USA) Sep-Pak C₁₈ cartridge.

A Dionex DX300 (Sunnyvale, CA, USA) IC (500-μl loop) equipped with AG11 and AS11

columns (4 mm diameter) was used with isocratic 0.10 M NaOH (aq.) at 1.00 ml min^{-1} with suppressed conductivity detection (Jackson et al., 1999; Wirt et al., 1998).

To prepare a sample for electrospray ionization mass spectrometry (ESI-MS), a 5.0-ml aliquot of dry twig 20 g dl^{-1} filtrate was run through six C_{18} cartridges. The IC was operated in preparative mode (2.00-ml loop). The eluate was collected from 7.1 to 9.0 min. This collected fraction of eluate was reinjected in its entirety using the same sample loop, and the peak at 8 min (ClO_4^-) was collected.

Complexation ESI-MS has been applied to water samples (Magnuson et al., 2000a,b; Urbansky and Magnuson, 2000; Urbansky et al., 2000). Perchlorate forms a stable ion pair with a quaternary ammonium cation. This complex is extracted into CH_2Cl_2 and injected without separation. The following were added to the collected fraction: 50 μl of 0.20 M $\text{C}_{10}\text{H}_{21}\text{N}(\text{CH}_3)_3\text{Br}(\text{aq.})$ solution (Fluka, Buchs, Switzerland) and 300 μl of CH_2Cl_2 (J.T. Baker Ultra Resi-analyzed, Phillipsburg, NJ, USA). After extraction, the CH_2Cl_2 phase was drawn off with a syringe. Aliquots of 25 μl were injected into the ESI-MS system as described (Magnuson et al., 2000a,b).

3. Results and discussion

Chromatograms for preparative and analytical IC are shown in Fig. 1. Negative ion ESI-MS signals at m/z 380 and 400 μm correspond to $\text{C}_{10}\text{H}_{21}\text{NMe}_3(\text{Br})(\text{ClO}_4)^-$ and $\text{C}_{10}\text{H}_{21}\text{NMe}_3(\text{ClO}_4)_2^-$, respectively. Peaks for the two ions are shown in Fig. 2. The average signal-to-blank ratio (S/B) using the sum, $(A_{380u} + A_{400u})$, was 4.2. Even separately, $(S/B)_{380u} = 4.9$ and $(S/B)_{400u} = 2.1$, either of which confirms the identification.

The 1:6 v/v dilution of the 20-g dl^{-1} filtrate of the submerged stalks was found to contain $10 \mu\text{g ml}^{-1}$ by IC, while that of the dry twigs was found to contain 200 ng ml^{-1} . These concentrations should be viewed as minima. There is no standard material by which to gauge the effectiveness of the leaching procedure; therefore, this preliminary finding is limited by the state of the science.

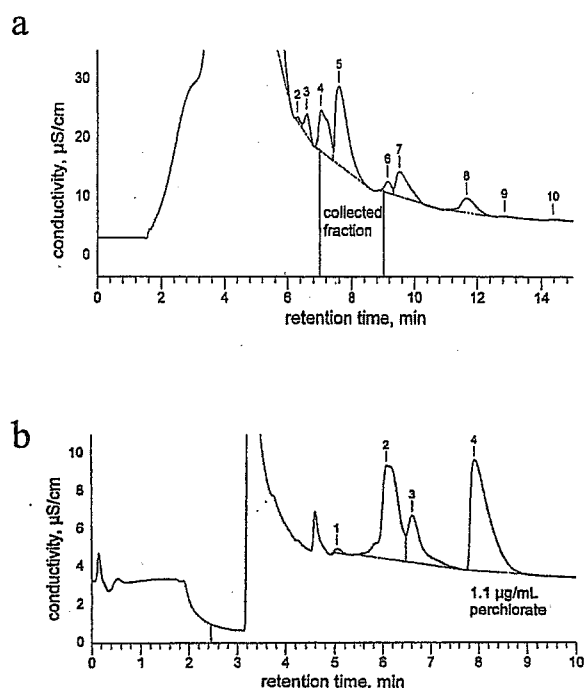


Fig. 1. (a) Preparative ion chromatograph of the 20 g dl^{-1} filtrate of dormant, dry (above water level) *Tamarix ramosissima* twigs. Peak 5 is perchlorate. Injection was made using a 2-ml sample loop. The fraction from 7 to 9 min was collected and reinjected for analysis. (b) Analytical ion chromatograph of the 7–9-min collected fraction of eluate from Fig. 1. Peak 4 is the perchlorate peak. Injection was made using a 2-ml sample loop. The fraction from 7.9 to 9.2 min was collected. The identification of perchlorate was confirmed by complexation electrospray ionization mass spectrometry (cESI-MS). The perchlorate was extracted into dichloromethane using decyltrimethylammonium cation (see Fig. 2 and text for more details).

No difference was observed between the clean-up cartridges, suggesting that perchlorate is not retained.

Submerged samples contained $300 \mu\text{g g}^{-1}$, while exposed samples contained $5\text{--}6 \mu\text{g g}^{-1}$. It is difficult to draw a conclusion about rate and selectivity of uptake in *T. ramosissima*, but it is clear that immersed stalks can absorb/adsorb significant amounts. Perhaps this could be exploited for remediation. Perchlorate-reducing microorganisms, especially facultative anaerobic bacteria are readily cultured in the laboratory (Coates et al., 2000; Giblin et al., 2000; Logan,

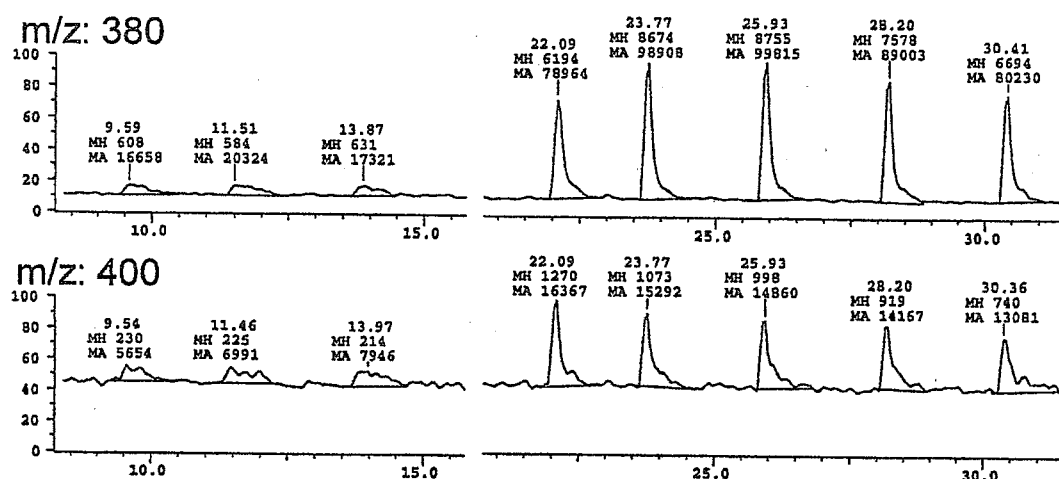


Fig. 2. Confirmation of perchlorate by negative ion complexation ESI mass spectrum obtained by extracting peak 4, which was collected from eluate in Fig. 2, with a cationic surfactant (decyltrimethylammonium bromide) into dichloromethane. Both the bromoperchlorato and bis(perchlorato) complex anions are observed in the mass spectrum. $C_{10}H_{21}NMe_3(Br)(ClO_4)^-$ has $m/z = 380$ u; $C_{10}H_{21}NMe_3(ClO_4)_2^-$ has $m/z = 400$ u. The first three injections are the blank (extract of IC eluate of just eluent after going through the suppressor). The last five injections are the dichloromethane extract of peak 4. Injection volume was 25 μ l.

1998). Phytoremediation of perchlorate by willows (genus *Salix*) has been reported by Nzengung and Wang (1998). Because significant incorporation of perchlorate would be expected with long-term rather than short-term or one-time exposure, diel fluctuations in concentrations may be averaged out, providing a more uniform measure of exposure as a biological indicator.

4. Conclusions

For better or worse, salt cedar must now be regarded as a major part of the ecosystem in the American Southwest and certainly in the Las Vegas Wash. Accordingly, plans to eradicate *Tamarix* must be evaluated in terms of total ecological impact, including effects on aqueous phase pollutants, such as perchlorate. It is not possible at this time to state what effect *Tamarix* has on perchlorate distribution in the Las Vegas Wash. Only two things are known for certain: *Tamarix* consumes an enormous amount of water and *Tamarix* can take up perchlorate.

Several lines of research are suggested by these facts. It may be possible to use *Tamarix* to concentrate the highly soluble perchlorate salts as part of a remediative strategy at some sites or to accumulate it in the wood. On the other hand, high rates of transpiration in salt cedar may make the perchlorate concentrations in ground water higher if perchlorate ion is selectively excluded when water is taken into the root system. Consequently, it will be important to answer the following questions: (1) Do tamarisks absorb all of the perchlorate along with the water they take in? (2) Do tamarisks secrete perchlorate salts on their leaves or retain them within the plant? (3) Can tamarisks harbor microbes in the rhizosphere that are capable of reducing perchlorate? (4) Do tamarisks metabolize (reduce) perchlorate to other oxyanions of chlorine or to chloride? (5) Can perchlorate levels found in tamarisk wood be used to assess long-term contamination of riparian ecosystems?

The nature, rate, and selectivity of perchlorate uptake and processing by salt cedar are all unknown, therefore, we cannot say whether this plant is improving or reducing water quality. Furthermore, without accurate information on the

transport and fate of perchlorate in *Tamarix*, the impact of eradication programs on perchlorate cannot be evaluated. Many programs rely on herbicides; however, any perchlorate in the plant is likely to be returned to the soil and ground water as the plant deteriorates and decomposes. This could potentially compound a problem if the salt cedar acts as a reservoir and the perchlorate is released upon the death of the plant. In order to ensure the protection of native species and the waterways and sound environmental management practices, it is necessary to completely understand the relationship among source water, salt cedar, and perchlorate in ecosystems such as the Las Vegas Wash.

Acknowledgements

We acknowledge Professor Jacimaria R. Batista (University of Nevada–Las Vegas) for assistance in procuring samples of salt cedar and Brenda Pohlmann (Nevada Division of Environmental Protection) for helpful discussions. Mention of specific brand names or models should not be construed to suggest endorsement or recommendation by the US government. This paper was produced by US government employees in the course of their official duties and is, therefore, exempt from copyright.

References

- Browner C. Part II. Environmental Protection Agency. 40 CFR parts 9, 141 and 142. Revisions to unregulated contaminant monitoring regulation for public water systems; final rule. Fed Regist 1999;64(180):50555–50620.
- Clark JJJ. Toxicology of perchlorate [Ch. 3 and references cited therein]. In: Urbansky ET, editor. Perchlorate in the environment. New York: Kluwer/Plenum, 2000.
- Coates JD, Michaelidou U, O'Connor SM, Bruce RA, Achenbach LA. The diverse microbiology of perchlorate reduction [Ch. 24 and references cited therein]. In: Urbansky ET, editor. Perchlorate in the environment. New York: Kluwer/Plenum, 2000.
- Damian P, Pontius FW. From rockets to remediation: the perchlorate problem. Environ Prot 1999;10:24–31.
- Deuser C, Haley J, Torrence I. Lake Mead 'SWAT' team attacks tamarisk. In Natural Resource Year in Review — 1997. National Park Service. Washington DC. Document No. D-1247, 1998.
- Environmental Protection Agency. Drinking Water Contaminant Candidate List. Document No. 815-F-98-002, 1998.
- Espenson JH. The Problem and perversity of perchlorate [Ch. 1]. In: Urbansky ET, editor. Perchlorate in the environment. New York: Kluwer/Plenum, 2000.
- Giblin TL, Herman DC, Frankenberger WT. An autotrophic system for the bioremediation of perchlorate from groundwater [Ch. 19, and references cited therein]. In: Urbansky ET, editor. Perchlorate in the environment. New York: Kluwer/Plenum, 2000.
- Jackson PE, Laikhtman M, Rohrer J. Determination of trace level perchlorate in drinking and ground water by ion chromatography. J Chromatogr A 1999;850:131–135.
- Logan BE. A review of chlorate- and perchlorate-respiring microorganisms. Biorem J 1998;2:81–95.
- Magnuson ML, Urbansky ET, Kelty CA. Determination of perchlorate at trace levels in drinking water by ion-pair extraction with electrospray ionization mass spectrometry. Anal Chem 2000a;72:25–29.
- Magnuson ML, Urbansky ET, Kelty CA. Microscale extraction of perchlorate in drinking water with low level detection by electrospray-mass spectrometry. Talanta; 2000b; 52:285–291.
- Muzika RM, Swearingen JM. National Park Service website, 1999. URL: <http://www.nps.gov/plants/alien/fact/tama1.htm>.
- Nzengung VA, Wang C. Influences on phytoremediation of perchlorate-contaminated water [Ch. 21 and references cited therein]. In: Urbansky ET, editor. Perchlorate in the environment. New York: Kluwer/Plenum, 2000.
- Perciasepe R. Part III. Environmental Protection Agency. Announcement of the drinking water contaminant candidate list; notice. Fed Regist 1998;63(40):10273–10287.
- Renner R. Perchlorate-tainted wells spur government action. Environ Sci Technol 1999;33:110A–111A.
- Urbansky ET. Perchlorate chemistry: implications for analysis and remediation. Biorem J 1998;2:81–95.
- Urbansky ET, Schock MR. Issues in managing the risks associated with perchlorate in drinking water. J Environ Manage 1999;56:79–95.
- Urbansky ET, Magnuson ML. Sensitivity and selectivity-enhancement in perchlorate anion quantitation using complexation-electrospray ionization-mass spectrometry [Ch. 8]. In: Urbansky ET, editor. Perchlorate in the environment. New York: Kluwer/Plenum, 2000.
- Urbansky ET, Gu B, Magnuson ML, Brown GM, Kelty CA. A survey of bottled waters for perchlorate using ion chromatography and electrospray ionization mass spectrometry. Submitted for publication. 2000.

Westbrooks R. Invasive Plants: Changing the Landscape of America — Factbook. Federal Interagency Committee for the Management of Noxious and Exotic Weeds. Washington DC, 1998. Available on the web; URL: <http://www.denix.osd.mil/denix/public/es-programs/conservation/invasive/deserts.html>.

Wirt K, Laikhtman M, Rohrer J, Jackson PE. Low level perchlorate analysis in drinking water and ground water by ion chromatography. *Am Environ Lab* 1998;10(1):5.

Wolff J. Perchlorate and the thyroid gland. *Pharm Rev* 1998;50:89–105.